EXPERIMENTAL AND NUMERICAL INVESTIGATION OF THE DIE SWELL PHENOMENON OF RUBBER BLENDS

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Abstract

Rubber profiles fabricated by means of extrusion are widely used in civil engineering, e.g., in pipeline constructions and for window sealings. The dimensioning of injection heads for the extrusion of rubber profiles is exclusively based on empiric knowledge of the non-linear flow behaviour of elastomers, basically of the so-called die swell. The swelling of the extrudate when emerging from a capillary is typical for non-Newtonian viscoelastic fluids. The viscosity of rubber blends is obtained by means of experiments with a capillary-viscometer. In this contribution it is shown how the die swell of a capillary experiment is computed by means of pressure measurements. For this objective information concerning the normal stress state in the capillary is required. Experiments with a torsion-viscometer allow a back calculation of the normal stress state and, thus, the computation of the die swell. An adaptation of the capillary-viscometer allows the experimental investigation of the die swell. Thus, a validation of the computed die swell can be realised.

Keywords

rubber blends, viscoelastic fluids, capillary-viscometry, rubber process analyzer.

1 Introduction

Capillary rheometry simulates polymer extrusion in a simplified way. It allows the characterisation of polymers by means of determination of the viscosity function and of the extrudate swell. The swelling of the extrudate when emerging from a capillary is typical for non-Newtonian viscoelastic fluids. Therefore, the experimental investigation and numerical treatment of the die swell is of high interest. This was one of the motivations for starting a research project in the field of rubber blend technologies. The knowledge of die swell phenomenon is important for manufacturing of rubber profiles. Thus, the final goal of this project is the numerical prognosis concerning tools for the extrusion of rubber.

The research work was performed in a co-operation with Semperit Technische Produkte Ges.m.b.H. & Co KG which provided the rubber blends as well as the experimental devices.

This paper is structured as follows: In Chapter 2 a short description of the used experimental devices is given. Chapter 3 refers to the used material law for the viscosity function. In Chapter 4 the results of the experimental investigation of the die swell are presented. It relates to the elastic properties of rubber blends. In Chapter 5 a condition is described how data from different experiments can be combined. Chapters 6 and 7 deal with the numerical simulation of the die swell after the exit from circular capillaries. The paper will be completed by conclusions and some present research activities.

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2 Experimental

The tested materials are non-vulcanised rubber blends used in industry, containing mainly EPDM (ethylene-propylene-diene-monomer) and carbon black in different compositions. So far four different rubber blends were investigated by means of experiments with steady and oscillatory shear loading. The materials are used for window sealings, pipeline constructions and various parts of cars.

The major test apparatus was a capillary-viscometer (HKV) manufactured by Göttfert Ges.m.b.H. (Germany). A laser scanning swell value measuring unit was installed at the end of the capillary. It measures the diameter of the strand immediately after its exit of the capillary by means of a laser beam with a wave-length of approximately 700 nm. In this contribution the dimensionless swell value χ_i represents a strand cross-sectional area ratio. It is defined as:

$$\chi_i = \left(\frac{d_i}{D} \right)^2 ,$$ (1)

where D is the diameter of the capillary and d_i is the diameter of the measured strand for the investigated duty point i. In the used capillary-viscometer the substance is pressed through a circular capillary with a certain stamp velocity v_i. A set of capillary dies with ratios of capillary length to capillary diameter, L/D, and diameters D was used. Extrusion rheology experiments for a sample were carried out at temperatures of 80 °C, 100 °C, and 120 °C.

Additional experiments were performed by means of a rubber process analyzer (RPA) from Alpha Technologies (United States). This torsion-viscometer strains a sample in shear by oscillating the lower die sinusoidally. Oscillation frequency has been set from 0.1 to 30 Hz. The RPA is designed to measure both elastic and viscous properties of elastomers and compounds. A complete description of this testing device has been summarised by (Dick et al 1999). After a certain procedure the storage modulus G' and the loss modulus G'' are provided.

With experiments with both the HKV and the RPA the investigation of various stamp velocities v_i and various angular frequencies ω_r, respectively, is possible. Therefore a vector notation is used. In this context j and s describe the total number of investigated duty points for a HKV and a RPA experiment, respectively.
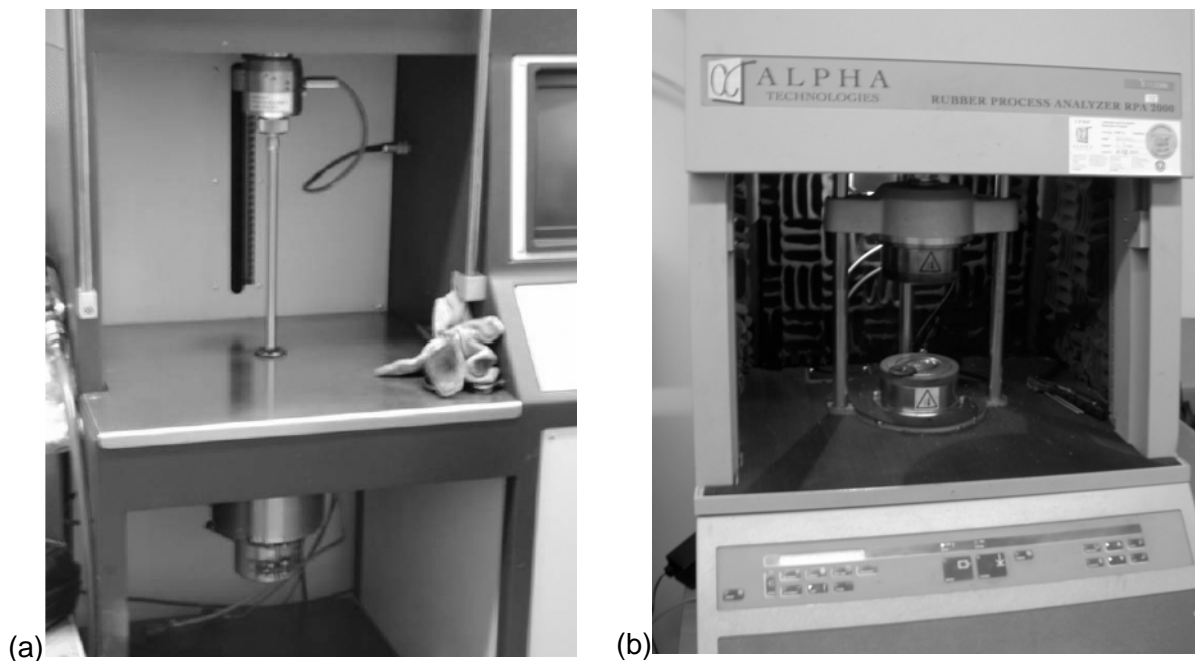

(a)   (b)

Figure 1 Used experimental devices (a) capillary-viscometer and (b) torsion-viscometer

3   Constitutive characterisation by means of a power law relationship

The viscosity η of rubber blends shows a clear dependence on the shear strain rate $\dot\gamma$. With increasing $\dot\gamma$ the viscosity η decreases. For the description of this so-called pseudo-plastic material behaviour of rubber blends the power law by Ostwald and de Waele in (Michaeli 2003) is used. Its application to the investigated rubber blends is possible for a common interval of the shear strain rate $\dot\gamma$. For the visualization of the obtained results a distinction is drawn between the flow curve $\tau(\dot\gamma)$ and the viscosity curve $\eta(\dot\gamma)$ (see Figure 2), where τ is the shear stress at the wall of the capillary. The power law approximates the results from the experiments by means of a straight line in the double logarithmic scale as:

$$\eta_i = k\,\dot\gamma_i^{\,n-1} \quad \Leftrightarrow \quad \tau_i = k\,\dot\gamma_i^{\,n} \quad \text{for} \quad i \in \{1,...,j\}, \tag{2}$$

where k is the consistency parameter in [Pas^n] and n is the dimensionless viscosity exponent. These parameters are determined by means of a Gaussian quadrature as:

$$n = \frac{j\sum_{i=1}^{j}\lg\tau_i\,\lg\dot\gamma_i - \sum_{i=1}^{j}\lg\tau_i\sum_{i=1}^{j}\lg\dot\gamma_i}{j\sum_{i=1}^{j}\lg^2\dot\gamma_i - \sum_{i=1}^{j}\lg\dot\gamma_i\sum_{i=1}^{j}\lg\dot\gamma_i} \quad \text{and} \quad \lg k = \frac{1}{j}\left(\sum_{i=1}^{j}\lg\tau_i - n\sum_{i=1}^{j}\lg\dot\gamma_i\right), \tag{3}$$

where k corresponds to the viscosity at a shear strain rate of $\dot\gamma = 1\ \text{s}^{-1}$ and n describes the slope of the viscosity curve in the corresponding diagram.
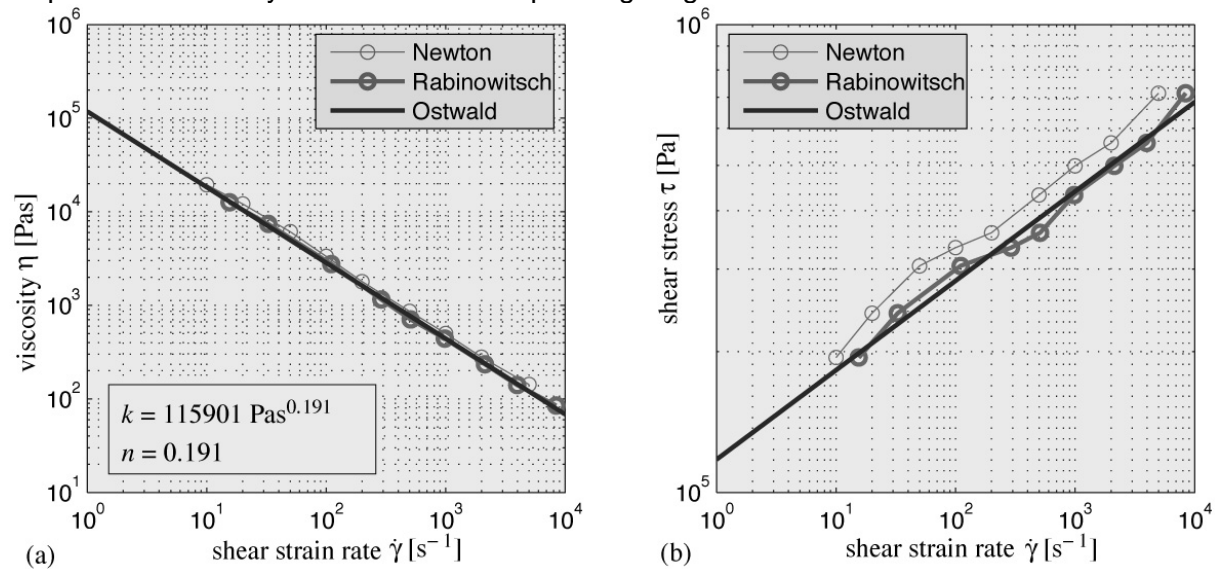

Figure 2 Application of the power law for a viscosity curve and a flow curve

Without die swell investigations the HKV experiment is used to determine the shear stress τ and the shear strain rate $\dot\gamma$. Thus, the viscosity curve is obtained. Various material characterisation methods are used in order to consider the non-linear coupling of the viscosity and the shear strain rate. So far, correction methods are used to obtain the viscosity curve for a non-Newtonian fluid, e.g. Rabinowitsch correction in (Michaeli 2003). Due to application problems of these correction methods for the investigated rubber blends (Müllner et al 2006) used a generalised Newton-Raphson procedure in order to obtain the viscosity curve. The successful validation of this method was done by (Müllner et al 2005) with a genetic algorithm.

4   Die swell of the investigated rubber blends

With the measured swell values various statements about the elastic behaviour of the investigated rubber blends are possible. From the rheological point of view the die swell occurs as a result of the recovery of the elastic deformation imposed in the capillary.
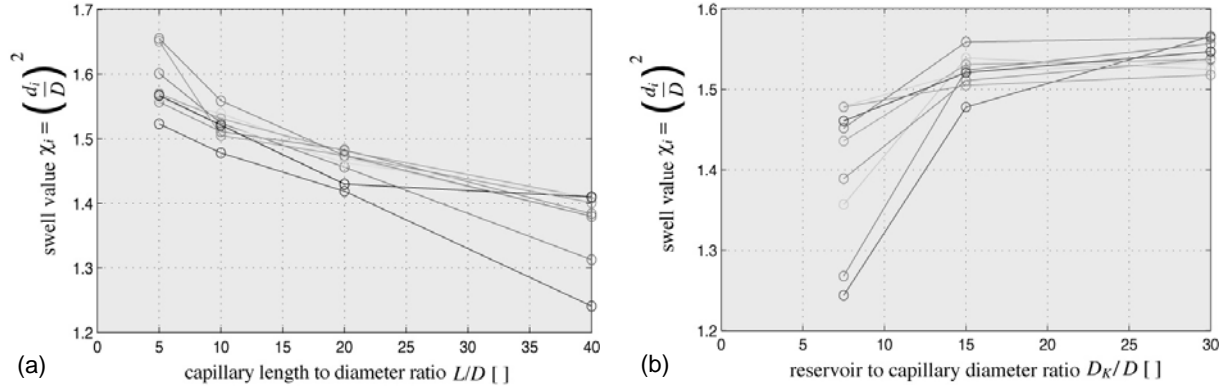
Figure 3 Die swell ratio versus (a) ratios of capillary length to capillary diameter (b) ratio of reservoir diameter to capillary diameter at a temperature of T = 100 °C

Figure 3 (a) shows that the value of the swell value χ decreases rapidly at low values of L/D and then levels off as L/D is increased further. Each line represents one duty point at a constant shear strain rate $\dot{\gamma}$. This behaviour of die swell indicates that the elastic behaviour of the melt depends on the residence time of the melt in the capillary. According to (Bagley et al 1963), this can also be interpreted as a decaying memory of the melt.

In Figure 3 (b) it is shown that the swell value χ increases at first with D_K/D and then levels off as D_K/D is increased further. The dependence of the swell value χ on the ratio of reservoir diameter D_K to capillary diameter D is particularly interesting because it indicates that the amount of stored elastic energy in the melt depends on the reservoir diameter up to a certain value, at which the conical zone of the converging flow streamlines into the capillary becomes unaffected from the reservoir wall. This fact certifies that extrudate swell results from the recoverable elastic energy stored in the melt, which originates from the large pressure drops at the entrance to the capillary. Both statements have been observed by (Han 1976) for polymers. For the numerical simulation of the die swell information concerning the normal stress state in the capillary are required. As reported by (Han 1976) the die swell depends on the recoverable shear strain

$$\gamma_{el,i} = \frac{\Delta\sigma_i}{2\tau_i} = \frac{\sigma_{11,i} - \sigma_{22,i}}{2\tau_i} \quad \text{for} \quad i \in \{1,...,j\} \ , \tag{4}$$

where $\Delta\sigma$ is the so-called first normal stress difference in the capillary and τ is the shear stress at the wall of the capillary. It is well known that for modelling the die swell only the difference between the first and the second component of the normal stress must be known. σ_{11} represents the normal stress in the flow direction and σ_{22} represents the normal stress in the direction of velocity change. With a HKV experiment only the determination of the shear stress is possible. The first normal stress difference has to be determined by means of a RPA-experiment.

5 Condition for an admissible combination of experimental data

In order to use the experimental results from the RPA for the modelling of the die swell from a HKV experiment a comparison of the viscosity functions obtained from both experiments is required. Therefore, an assumption concerning the investigated duty points of both experiments is necessary. Duty points of the HKV experiment are characterised by stamp velocities v_i, duty points of the RPA experiments by angular frequencies ω_r.

For the described objective the relationship by (Cox and Merz 1958) can be used. This condition establishes a relationship between the absolute value of the complex viscosity $\left|\eta^*(\omega)\right|$ and the stationary dynamic viscosity $\eta(\dot{\gamma})$ obtained from continuous shear. The Cox-Merz relationship is defined as:

$$\left|\eta^*(\omega)\right| = \eta(\dot{\gamma}) \quad \text{for} \quad \dot{\gamma}_i = \omega_r \ . \tag{5}$$

That is, the absolute value of the complex viscosity corresponds with the stationary viscosity, when the numerical value of the angular frequency $\omega_r \left(r \in \{1,...,s\} \right)$ is equal to the shear strain rate $\dot{\gamma}_i \left(i \in \{1,...,j\} \right)$. For many polymers the validity of this relationship has been proven.

The validity of this relationship for the investigated rubber blends is proven in this chapter. The absolute value of the complex viscosity is defined as:

$$\left| \mathbf{\eta}^* \right| = \frac{\left| \mathbf{G}^* \right|}{\omega} \ ,$$
(6)

where

$$\left| G_r^* \right| = \sqrt{G_r^{'2} + G_r^{''2}}$$
(7)

is the complex shear modulus obtained using storage modulus G' and loss modulus G'' of a RPA experiment with the same material.

Figure 4 (a) shows the viscosity curves $\left| \eta^* (\omega) \right|$ obtained using storage and loss modulus as well as the viscosity curves $\eta(\dot{\gamma})$ obtained by means of a HKV experiment. The full lines were obtained at a temperature of 80 °C, the dashed lines at 100 °C and the dash-dotted lines at a temperature of 120 °C. In the figure, e. g., the results of the capillary L/D = 40/2 mm for the HKV experiment are shown.
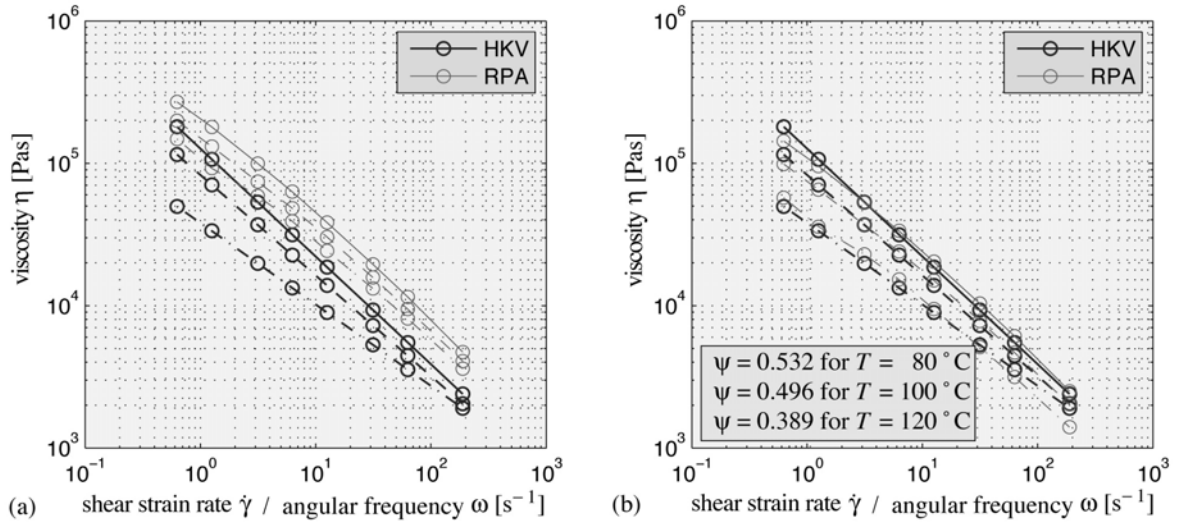

Figure 4 Comparison of viscosity curves obtained by means of a HKV and
a RPA experiment (a) without and (b) with scaling factor ψ for a typical rubber blend

Figure 4 (a) shows that the Cox-Merz relationship is not applicable to the investigated rubber blends. However, the slope of the viscosity curves is portrayed correctly. Therefore, the different viscosity curves can be correlated by the introduction of a scaling factor ψ. This scaling factor is defined as

$$\psi = \frac{1}{s} \sum_{r=1}^{s} \frac{\eta\left(\dot{\gamma}_i = \omega_r\right)}{\left| \eta^* (\omega_r) \right|} \ .$$
(8)

Using (2) for the dynamic viscosity and (6) for the complex viscosity one can simplify equation (8) as

$$\psi = \frac{k}{s} \sum_{r=1}^{s} \frac{\omega_r^n}{\left| G_r^* \right|} \ .$$
(9)

The power law constants k and n are obtained from (3) using the data of the corresponding HKV experiment. By multiplication of the complex viscosity $\left| \eta^* (\omega) \right|$ with the scaling factor ψ a correspondence between the viscosity curves has been achieved. For the capillary L/D = 40/2 mm this is shown, e. g., in Figure 4 (b). The obtained scaling factors decrease with increasing melt temperature.

6 Calculation of the first normal stress difference

By introducing the scaling factor ψ the Cox-Merz relationship can be used for the investigated rubber blends.

For various polymers (Laun 1986) found an empirical equation for the first normal stress difference. With a proven validity of the Cox-Merz relationship for any material the normal stress state can be obtained with following empirical equation. Under consideration of the scaling factor according to (9) the normal stress state in a capillary can be gathered from:

$$\Delta\sigma_r = 2\,\psi\,G_r{'}\left[1+\left(\frac{G_r{'}}{G_r{''}}\right)^2\right]^{0.7} \quad \text{for} \quad r \in \{1,...,s\} \ .\tag{10}$$

(Wen et al 2004) have chosen another way of using (10). By variation of the power law index 0.7 in (10) the application of this empirical equation has been proven for polymer fluids. This approach is not used for the investigated rubber blends in order to minimise the number of material parameters.

The validation of (10) for the herein considered rubber blends is done by means of a comparison with the results of the experimental determination of the die swell. With the relationship by (Tanner 1970)

$$\Delta\sigma_i = 2\,\tau_i\,\sqrt{2\,\chi_i^{\,3}-2}\tag{11}$$

and the relationship by (Bagley and Duffey 1970)

$$\Delta\sigma_i = 2\,\tau_i\,\sqrt{\chi_i^{\,2}-\chi_i^{-1}}\tag{12}$$

the first normal stress difference is obtained using the experimental data of the die swell of the corresponding HKV experiment. As basis for these observations equation (4) is used.
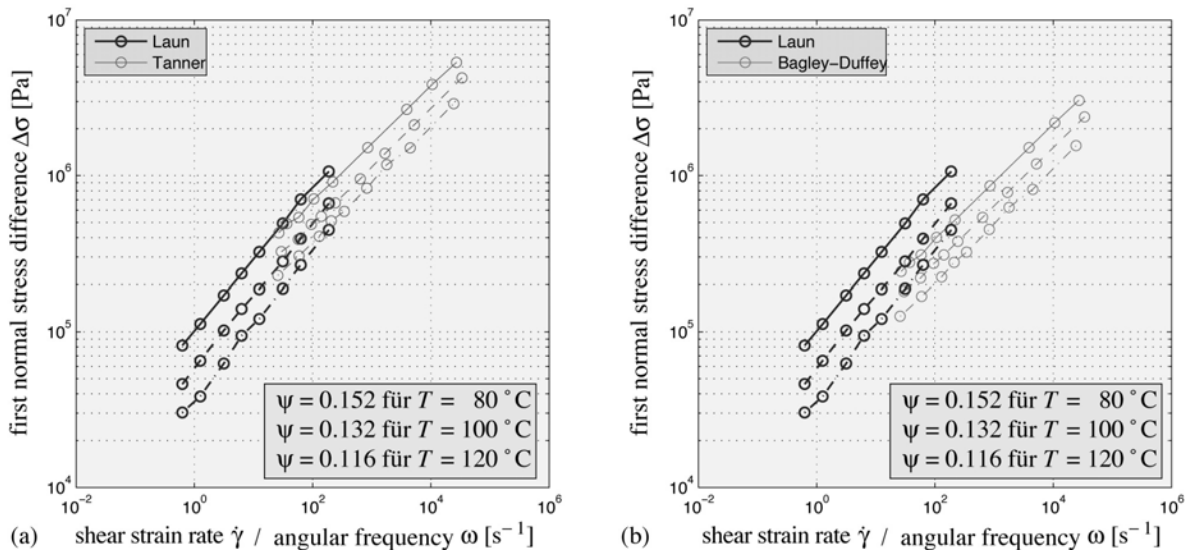

Figure 5 Validation of the onsets by (a) (Tanner 1970) and (b) (Bagley and Duffey 1970) by means of the empirical equation by (Laun 1986) for a typical rubber blend

In Figure 5 the results of the validation of the first normal stress difference are shown, e. g., for the capillary L/D = 2.5/0.5 mm for a HKV-experiment. As in Figure 4, the results of three different investigated temperatures are shown. $\Delta\sigma$, calculated by (10), correlates better with the onset of (Tanner 1970) as shown in Figure 5 (a). Nevertheless, this comparison leads to a sufficient validation for the combination of HKV and RPA experiments.

With the chosen approach no further material parameters are required. The scaling factor ψ is automatically determined when comparing the experimental data of both the HKV and the RPA experiment. According to (Müllner et al 2005) the onset of (Tanner 1970) can be used for the modelling of rubber blends, which consist mainly of EPDM and carbon black in different compositions.

7 Calculation of the die swell using RPA-experiments

It has been shown that the first normal stress difference $\Delta\sigma$ can be calculated by means of the empirical equation by (Laun 1986). With the relationship by (Tanner 1970) the die swell for circular capillaries can be obtained. Dissolving (11) for the swell value χ_i leads to

$$\chi_i = \sqrt[3]{1 + \frac{1}{2}\gamma_{el,i}{}^2} = \sqrt[3]{1 + \frac{1}{2}\left(\frac{\Delta\sigma_i}{2\tau_i}\right)^2} \quad , \tag{13}$$

where the dependence of the die swell on the recoverable shear strain is considered according to (4). Using (10) for $\Delta\sigma$ and τ according to the characterisation methods mentioned in Chapter 3 one can calculate the die swell for the corresponding HKV-experiment. In order to compare the results from the different approaches a regression analysis for the swell value similar to (Liang 2004) is done as:

$$\chi_i = \beta_1 + \beta_2 \lg\dot{\gamma}_i \quad , \tag{14}$$

where β_1 and β_2 are constants characterising the elastic properties of the material. Similar to the power law constants the parameters β_1 and β_2 are obtained by means of a Gaussian quadrature according to (3). β_1 corresponds to the swell value at a shear strain rate of $\dot{\gamma}$ = 1 s^{-1}.

Figure 6 shows the comparison of measured and calculated swell values for the HKV experiment L/D = 20/1 mm at a melt temperature of T = 120 °C. The figure also contains the parameters β_1 and β_2 of both the measured and the back calculated swell values according to (13).

The agreement between measured and back calculated swell value is good, especially in the overlapping range of both approaches. The different ranges for the shear strain rate and the angular frequency occur, because of the different experiments.

Comparing the scale of the die swell on the ordinate of Figure 6 a value of $\Delta\chi$ = 0.1 corresponds with the changing of the strand diameter Δd = 0.046 mm for the contemplated HKV experiment L/D = 20/1 mm.
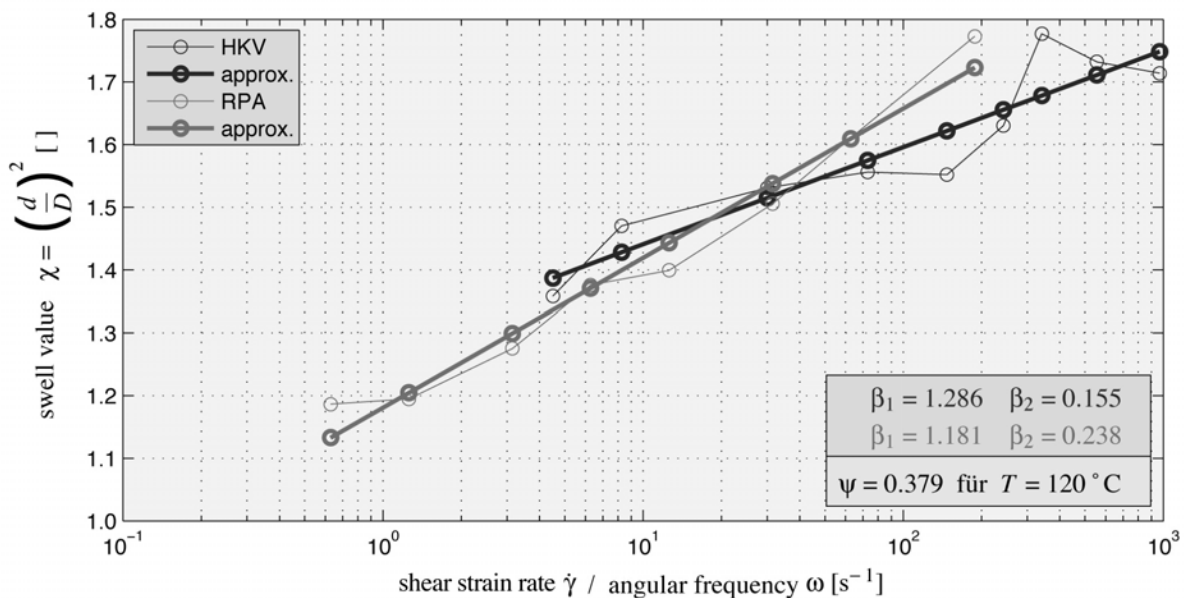

Figure 6 Calculated and measured swell value for a typical rubber blend

The investigations of other rubber blends have shown that the described procedure is not applicable for all capillary experiments. When the scaling factor reaches a value of $\psi < 0.1$ no satisfying agreement for the first normal stress difference is obtained.

However, it was one goal of this contribution to introduce no new material and process parameters, respectively, for the simulation of the experimental determined die swell for the investigated rubber blends.

8   Conclusions

The published methods for the constitutive characterisation and the identification of the swelling behaviour are well suitable for polymers. Its application for rubber blends used in industry is not always reasonable. In the context of die swell phenomena this contribution deals with the combination of experimental data of two common experimental devices. With the Cox-Merz relationship the identification of a scaling factor was possible. This approach allows the computation of the die swell of rubber blends due to a flow through circular capillaries.

The required information concerning the normal stress state is achieved with an empirical equation by (Laun 1986) and the identified scaling factor. The application of this equation for the investigated rubber blends was successful proven by means of an experimental investigation of the die swell after the exit of a die through a capillary of a HKV experiment. The presented method does not require any new material parameters which are unknown for new materials. The scaling factor is automatically computed when using the Cox-Merz relationship. The obtained results will be used to improve the numerical simulation of die swell phenomenon and its influence on rubber profile geometry. This will lead to better results for the simulation of injection heads.

9   Acknowledgements

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